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3, rue de la Harpe, 1205, Genève, Suisse  
P.O. Box 6809, 1211, Genève, Suisse  
P.O. Box 17, 2200, La Haye, Pays-Bas  
P.O. Box 17, 2200, La Haye, Pays-Bas

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- (71) Applicant (for all designated States except US): JOHNSON MATTHEY PLC [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): LINDALL, Charles, Mark [GB/GB]; 23 Falcon Lane, Crooksbarrow, Norton, Stockton on Tees TS20 1LS (GB). RIDLAND, John [GB/GB]; 12 Oatlands Way, Durham, County Durham DH1 5GL (GB). SLACK, Neville [GB/GB]; 139 Station Road, Billingham, Stockton on Tees, Cleveland TS23 2RL (GB).
- (74) Agents: GIBSON, Sara, Hillary, Margaret et al.; Syntex Intellectual Property Dept., Belasis Avenue, P.O. Box 1, Billingham, Cleveland TS23 1LB (GB).
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(54) Title: CATALYST AND PROCESS FOR PREPARATION OF AN ESTER

(57) Abstract: A catalyst composition suitable for use as a catalyst for the preparation of an ester comprises an organometallic compound which is the reaction product of an alkoxide or condensed alkoxide of at least one metal selected from titanium, zirconium or aluminium, an alcohol containing at least two hydroxyl groups, a base and an organophosphorus compound of general formula  $PX(OR^1)_a(R^2)_b$  where X is S or O,  $R^1$  is alkyl/aryl, substituted alkyl/aryl, ether-alkyl, alkoxy,  $-COR^3$  where  $R^3$  is (optionally substituted)  $C_{1-6}$  alkyl or carboxylic acid (or derivative thereof),  $-(CH_2)_xCOOR^4$ , where  $R^4$  is alkyl, preferably  $C_{1-6}$  alkyl and x is preferably 1-3; each  $R^2$  is independently H, alkyl/aryl, substituted alkyl/aryl, ether-alkyl, e.g. polyoxyalkyl, especially polyoxyethyl or polyoxypropyl, alkoxy,  $-OCOR^3$  where  $R^3$  is (optionally substituted)  $C_{1-6}$  alkyl or carboxylic acid (or derivative thereof),  $-(CH_2)_xCOOR^4$ , where  $R^4$  is alkyl, preferably  $C_{1-6}$  alkyl and x is preferably 1-3; at least one of  $R^1$  and  $R^2$  contains a donor group which is capable of coordinating to or forming a covalent bond with the metal, a is in the range 1-3, b is in the range 0-2 and  $a + b = 3$ .

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## CATALYST AND PROCESS FOR PREPARATION OF AN ESTER

The invention concerns catalyst compositions and in particular catalyst compositions which comprise novel organotitanium, organozirconium or organoaluminium compounds containing phosphorous which are useful catalysts for esterification reactions.

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Organotitanium compounds and, in particular, titanium alkoxides or alkoxydes are known as catalysts for esterification processes. During the esterification, these compounds are frequently converted to insoluble compounds of titanium which result in a hazy product. The presence of a haze is a particular disadvantage in polyesters which have a high viscosity and/or high melting point and are therefore difficult to filter. Furthermore, many organotitanium compounds which are effective catalysts in the manufacture of polyesters such as polyethylene terephthalate are known to produce unacceptable yellowing in the final polymer. GB-A-2 314 081 relates to an esterification process in which these problems are partially solved but there is still a need for a catalyst system which induces little or no yellowing in a polyester produced using the catalyst. Furthermore, there is a need for a catalyst which produces polyester which is heat stable in the melt.

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It is an object of the present invention to provide an improved catalyst system for a process for preparing esters.

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According to the invention, a catalyst composition suitable for use as a catalyst for the preparation of an ester comprises an organometallic compound which is the reaction product of

- i. an alkoxide or condensed alkoxide of at least one metal selected from titanium, zirconium or aluminium,
- ii. an alcohol containing at least two hydroxyl groups,
- iii. a base and
- iv. an organophosphorus compound of general formula  $PX(OR^1)_a(R^2)_b$  where X is S or O,  $R^1$  is alkyl/aryl, substituted alkyl/aryl, ether-alkyl, alkoxy,  $-C(O)R^3$  where  $R^3$  is (optionally substituted)  $C_{1-6}$  alkyl or carboxylic acid (or derivative thereof),  $-(CH_2)_xCOOR^4$ , where  $R^4$  is alkyl, preferably  $C_{1-6}$  alkyl and x is preferably 1 – 3; each  $R^2$  is independently H, alkyl/aryl, substituted alkyl/aryl, ether-alkyl, e.g. polyoxyalkyl, especially polyoxyethyl or polyoxypropyl, alkoxy,  $-OCOR^3$  where  $R^3$  is (optionally substituted)  $C_{1-6}$  alkyl or carboxylic acid (or derivative thereof),  $-(CH_2)_xCOOR^4$ , where  $R^4$  is alkyl, preferably  $C_{1-6}$  alkyl and x is preferably 1 – 3; at least one of  $R^1$  and  $R^2$  contains a donor group which is

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capable of coordinating to or forming a covalent bond with the metal, a is in the range 1 – 3, b is in the range 0 – 2 and  $a + b = 3$ .

Also according to the invention, a process for the preparation of an ester comprises carrying out an esterification reaction in the presence of a catalyst composition comprising an organometallic compound which is the reaction product of:-

- i. an alkoxide or condensed alkoxide of at least one metal selected from titanium, zirconium or aluminium,
- ii. an alcohol containing at least two hydroxyl groups,
- 10 iii. a base and
- iv. an organophosphorus compound of general formula  $PX(OR^1)_a(R^2)_b$  where X is S or O,  $R^1$  is alkyl/aryl, substituted alkyl/aryl, ether-alkyl, alkoxy,  $-C(O)R^3$  where  $R^3$  is (optionally substituted)  $C_{1-8}$  alkyl or carboxylic acid (or derivative thereof),  $-(CH_2)_xCOOR^4$ , where  $R^4$  is alkyl, preferably  $C_{1-6}$  alkyl and x is preferably 1 – 3; each  $R^2$  is independently
- 15 H, alkyl/aryl, substituted alkyl/aryl, ether-alkyl, e.g. polyoxyalkyl, especially polyoxyethyl or polyoxypropyl, alkoxy,  $-OCOR^3$  where  $R^3$  is (optionally substituted)  $C_{1-8}$  alkyl or carboxylic acid (or derivative thereof),  $-(CH_2)_xCOOR^4$ , where  $R^4$  is alkyl, preferably  $C_{1-6}$  alkyl and x is preferably 1 – 3; at least one of  $R^1$  and  $R^2$  contains a donor group which is capable of coordinating to or forming a covalent bond with the metal, a is in the range 1 –
- 20 3, b is in the range 0 – 2 and  $a + b = 3$ .

In a further embodiment the organometallic compound suitable for use in an esterification process further comprises a 2-hydroxy carboxylic acid.

- 25 The organometallic compound comprises the reaction product of an alkoxide (also known as an orthoester) or condensed alkoxide (or orthoester) of at least one metal selected from titanium, zirconium or aluminium. Normally an alkoxide or condensed alkoxide of one of the selected metals is used but it is within the scope of the invention to use an alkoxide or condensed alkoxide of more than one of the selected metals. For clarity we refer hereinafter
- 30 to a titanium, zirconium or aluminium alkoxide or condensed alkoxide, and all such references should be taken to include alkoxides or condensed alkoxides of more than one metal, e.g. to a mixture of titanium and zirconium alkoxides.

- Preferably, the alkoxide has the formula  $M(OR)_4$  or  $Al(OR)_3$  where M is titanium or zirconium
- 35 and R is an alkyl group. More preferably R contains 1 to 6 carbon atoms and particularly

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suitable alkoxides include tetraisopropoxy titanium, tetra-n-butoxy titanium, tetra-n-propoxy zirconium, tetra-n-butoxy zirconium and tetra-iso-butoxy aluminium. The condensed alkoxides suitable for preparing the organometallic compounds used in this invention are typically prepared by careful hydrolysis of titanium, zirconium or aluminium alkoxides. Titanium or zirconium condensed alkoxides are frequently represented by the formula  $RO[M(OR)_2O]_nR$  in which R represents an alkyl group and M represents titanium or zirconium. Preferably, n is less than 20 and more preferably is less than 10. Preferably, R contains 1 to 12 carbon atoms, more preferably, R contains 1 to 6 carbon atoms and useful condensed alkoxides include the compounds known as polybutyl titanate, polyisopropyl titanate and polybutyl zirconate.

Preferably, the alcohol containing at least two hydroxyl groups is a dihydric alcohol and can be a 1,2-diol such as 1,2-ethanediol or 1,2-propanediol, a 1,3-diol such as 1,3-propanediol, a 1,4-diol such as 1,4-butanediol, a diol containing non-terminal hydroxyl groups such as 2-methyl-2,4-pentanediol or a dihydric alcohol containing a longer chain such as diethylene glycol or a polyethylene glycol. Preferred dihydric alcohols include 1,2-ethanediol, 1,3-propanediol and 1,4-butanediol. The organometallic compound can also be prepared from a polyhydric alcohol such as glycerol, trimethylolpropane or pentaerythritol.

Preferably, the organometallic compound is prepared by reacting a dihydric alcohol with an alkoxide or condensed alkoxide in a ratio of from 1 to 32 moles of dihydric alcohol to each mole of titanium, zirconium or aluminium. More preferably, the reaction product contains 2 to 25 moles of dihydric alcohol per mole of titanium, zirconium or aluminium and most preferably 4 to 25 moles dihydric alcohol per mole of titanium, zirconium or aluminium.

The organophosphorus compound of general formula  $PX(OR^1)_a(R^2)_b$  where X is S or O,  $R^1$  is alkyl/aryl, substituted alkyl/aryl, ether-alkyl, alkoxy,  $-OCOR^3$  where  $R^3$  is (optionally substituted)  $C_{1-6}$  alkyl or carboxylic acid (or derivative thereof),  $-(CH_2)_xCOOR^4$ , where  $R^4$  is alkyl, preferably  $C_{1-6}$  alkyl and x is preferably 1 – 3; each  $R^2$  is independently H, alkyl/aryl, substituted alkyl/aryl, ether-alkyl, e.g. polyoxyalkyl, especially polyoxyethyl or polyoxypropyl, alkoxy,  $-OCOR^3$  where  $R^3$  is (optionally substituted)  $C_{1-6}$  alkyl or carboxylic acid (or derivative thereof),  $-(CH_2)_xCOOR^4$ , where  $R^4$  is alkyl, preferably  $C_{1-6}$  alkyl and x is preferably 1 – 3; at least one of  $R^1$  and  $R^2$  contains a donor group which is capable of coordinating to or forming a covalent bond with the metal, a is in the range 1 – 3, b is in the range 0 – 2 and  $a + b = 3$ .

X is preferably O.

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The donor group is preferably S, O, N, OH, NH or SH; particularly preferred are O, OH or NH. When R<sup>1</sup> and /or R<sup>2</sup> is alkyl, or alkoxy then they are preferably C<sub>1-6</sub> alkyl or alkoxy, e.g. ethyl, propyl or butyl or ethoxy, propoxy or butoxy. When R<sup>1</sup> and /or R<sup>2</sup> is substituted alkyl or alkoxy  
5 then they are preferably OH- or NH- substituted C<sub>1-10</sub> alkyl or alkoxy groups, for example hydroxypropyl, hydroxyethyl, hydroxymethyl, hydroxypropoxy or hydroxyethoxy, aminopropyl, aminoethyl, aminomethyl, aminopropoxy or aminoethoxy.

When R<sup>1</sup> and /or R<sup>2</sup> is ether-alkyl it is preferably polyoxyalkyl, especially polyoxyethyl or  
10 polyoxypropyl, i.e. it is preferably derived from a polyethylene glycol or polypropylene glycol moiety. Alternatively it is derived from a simple glycol such as ethylene glycol to form a hydroxy-ether group.

When R<sup>1</sup> and /or R<sup>2</sup> is -OCOR<sup>3</sup> where R<sup>3</sup> is (optionally substituted) C<sub>1-6</sub> alkyl or carboxylic acid  
15 (or derivative thereof), then the phosphorus atom is joined via an ester link to a carboxyl-containing compound. A preferred example of such a compound is a residue of a hydroxy carboxylic acid such that the organophosphorus compound is a phosphorus derivative of a hydroxycarboxylic acid such as lactic, citric, tartaric or malic acids for example.

When R<sup>1</sup> and /or R<sup>2</sup> is -(CH<sub>2</sub>)<sub>x</sub>COOR<sup>4</sup> then R<sup>4</sup> is preferably C<sub>1</sub> - C<sub>6</sub> alkyl and x is preferably 1  
20 - 3. A preferred example of such a compound when R<sup>2</sup> is -(CH<sub>2</sub>)<sub>x</sub>COOR<sup>4</sup> is a phosphonoacetate, for example an ethyl phosphonoacetate when x is 1 and R<sup>4</sup> is ethyl.

Preferred organophosphorus compounds include phosphite diesters, phosphate triesters and  
25 phosphonate diesters. Examples of preferred compounds include triethylphosphonoacetate (TEPA), and di(polyoxyethyl)hydroxymethylphosphonate which are phosphonate diesters.

The amount of organophosphorus compound present in the catalyst composition of the invention is usually in the range 0.1 to 4.0 mole of phosphorus to 1 mole of metal (titanium,  
30 zirconium or aluminium), preferably in the range 0.1 to 2.0 mole phosphorus to 1 mole metal and most preferably in the range 0.3 to 1.8 mole phosphorus to 1 mole metal.

Suitable inorganic bases include inorganic bases such as sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, calcium hydroxide and ammonium  
35 hydroxide. Preferred organic bases include quaternary ammonium compounds such as

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tetrabutyl ammonium hydroxide, tetraethyl ammonium hydroxide (TEAH), choline hydroxide (trimethyl(2-hydroxyethyl)ammonium hydroxide) or benzyltrimethyl ammonium hydroxide, or alkanolamines such as monoethanolamine, diethanolamine, triethanolamine and triisopropanolamine. Particularly preferred organic bases include choline hydroxide and  
5 TEAH, which have been found to produce polyester having particularly good colour properties when used in the catalysts of the invention. Usually, the amount of base used is in the range 0.1 to 4.0 mole base per mole of metal (titanium, zirconium or aluminium). The preferred amount is in the range 0.1 to 2.0 mole base per mole of metal and, frequently, the amount of base present is in the range 0.3 to 1.5 mole base per mole of titanium, zirconium or  
10 aluminium.

When 2-hydroxy carboxylic acids are used in the catalyst compositions of the invention, preferred acids used include lactic acid, citric acid, malic acid and tartaric acid. Some suitable acids are supplied as hydrates or as aqueous mixtures and can be used in this form. When a  
15 2-hydroxy acid is present, the preferred molar ratio of acid to titanium, zirconium or aluminium in the reaction product is 0.5 to 4 moles per mole of titanium, zirconium or aluminium. More preferably the reaction product contains 1.0 to 3.5 moles of 2-hydroxy acid per mole of titanium, zirconium or aluminium.

20 The organometallic compound can be prepared by mixing the components (alkoxide or condensed alkoxide, alcohol containing at least two hydroxyl groups, organophosphorus compound and base, with removal, if desired, of any by-product, (e.g. isopropyl alcohol when the alkoxide is tetraisopropoxytitanium), at any appropriate stage. In one preferred method the alkoxide or condensed alkoxide and a dihydric alcohol are mixed and, subsequently, a  
25 base is added, followed by the organophosphorus compound. When a 2-hydroxy carboxylic acid is also present in the reaction product, this is usually added to the alkoxide or condensed alkoxide before the organophosphorus compound is added. Alternatively, all or part of the 2-hydroxy carboxylic acid can be neutralised with the base and the resulting salt added to the other components of the reaction mixture, including, if desired, a further portion of the base.

30 The catalyst composition of the invention may additionally comprise a compound of germanium, antimony or tin and, in general, any compound can be used including mixtures of compounds of more than one of these metals. The preferred compound of germanium is germanium dioxide. Preferably, the antimony compound is antimony trioxide or a salt of  
35 antimony, for example antimony triacetate. A number of tin compounds are suitable, including

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salts, such as tin acetate and organotin compounds, such as dialkyl tin oxides, for example, dibutyl tin oxide, dialkyl tin dialkanoates, for example, dibutyl tin dilaurate and alkylstannoic acids, for example butylstannoic acid ( $C_4H_9SnOOH$ ).

- 5 The esterification reaction of the process of the invention can be any reaction by which an ester is produced. The reaction may be (i) a direct esterification in which a carboxylic acid or its anhydride and an alcohol react to form an ester or (ii) a transesterification (alcoholysis) in which a first alcohol reacts with a first ester to produce an ester of the first alcohol and a second alcohol produced by cleavage of the first ester or (iii) a transesterification reaction in which two esters are reacted to form two different esters by exchange of alkoxy radicals. Direct esterification or transesterification can be used in the production of polymeric esters and a preferred process of the invention comprises a polyesterification process.

- 15 Many carboxylic acids and anhydrides can be used in direct esterification including saturated and unsaturated monocarboxylic acids and anhydrides of such acids such as stearic acid, isostearic acid, capric acid, caproic acid, palmitic acid, oleic acid, palmitoleic acid, triacontanoic acid, benzoic acid, methyl benzoic acid, salicylic acid and rosin acids such as abietic acid, dicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, sebacic acid, adipic acid, azelaic acid, succinic acid, fumaric acid, maleic acid, naphthalene dicarboxylic acid and pamoic acid and anhydrides of these acids and polycarboxylic acids such as trimellitic acid, citric acid, trimesic acid, pyromellitic acid and anhydrides of these acids. Alcohols frequently used for direct esterification include aliphatic straight chain and branched monohydric alcohols such as butyl, pentyl, hexyl, octyl and stearyl alcohols, dihydric alcohols such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol and 1,6-hexanediol and polyhydric alcohols such as glycerol and pentaerythritol.

- 25 The esters employed in an alcoholysis reaction are generally the lower homologues such as methyl, ethyl and propyl esters since, during the esterification reaction, it is usual to eliminate the displaced alcohol by distillation. These lower homologue esters of the acids suitable for direct esterification are suitable for use in the transesterification process according to the invention. Frequently (meth)acrylate esters of longer chain alcohols are produced by alcoholysis of esters such as methyl acrylate, methyl methacrylate, ethyl acrylate and ethyl methacrylate. Typical alcohols used in alcoholysis reactions include butyl, hexyl, n-octyl and 2-ethyl hexyl alcohols and substituted alcohols such as dimethylaminoethanol.

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When the esterification reaction is a transesterification between two esters, generally the esters will be selected so as to produce a volatile product ester which can be removed by distillation.

- 5 As mentioned hereinbefore, polymeric esters can be produced by processes involving direct esterification or transesterification and a particularly preferred embodiment of the esterification process of the invention is a polyesterification reaction in the presence of the catalyst composition described hereinbefore. In a polyesterification reaction polybasic acids or esters of polybasic acids are usually reacted with polyhydric alcohols to produce a polymeric ester.
- 10 Linear polyesters are often produced from dibasic acids such as those mentioned hereinbefore or esters of said dibasic acids and dihydric alcohols. Preferred polyesterification reactions according to the invention include the reaction of terephthalic acid or dimethyl terephthalate with 1,2-ethanediol (ethylene glycol) to produce polyethylene terephthalate or with 1,3-propanediol (propylene glycol) to produce polypropylene terephthalate or with 1,4-
- 15 butanediol (butylene glycol) to produce polybutylene terephthalate or reaction of naphthalene dicarboxylic acid or dimethyl naphthalenate with 1,2-ethanediol to produce polyethylene naphthalate. Other acids, such as isophthalic acid and other glycols such as 1,6-hexanediol and polyhydric alcohols such as glycerol, trimethylolpropane and pentaerythritol are also suitable for preparing polyesters.

20

The esterification reaction of the invention can be carried out using any appropriate, known technique for an esterification reaction.

- 25 A typical process for the preparation of polyethylene terephthalate comprises two stages. In the first stage terephthalic acid or dimethyl terephthalate is reacted with 1,2-ethanediol to form a bis(hydroxyethyl)terephthalate prepolymer and the by-product water or methanol is removed. The prepolymer is subsequently heated in a second (polycondensation) stage to remove 1,2-ethanediol and form a long chain polymer. Either or both these stages may comprise an esterification process according to this invention.

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- In direct esterification the acid or anhydride and an excess of alcohol are typically heated, if necessary in a solvent, in the presence of the catalyst composition. Water is a by-product of the reaction and this is removed, as an azeotrope with a boiling mixture of solvent and/or alcohol. Generally, the solvent and/or alcohol mixture which is condensed is at least partially
- 35 immiscible with water which is therefore separated before solvent and/or alcohol are returned



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to the reaction vessel. When reaction is complete the excess alcohol and, when used, solvent are evaporated.

In view of the fact that the catalyst compositions of the invention do not normally form  
5 insoluble species, it is not generally necessary to remove them from the reaction mixture, as is frequently necessary with conventional catalysts. A typical direct esterification reaction is the preparation of bis(2-ethylhexyl) phthalate which is prepared by mixing phthalic anhydride and 2-ethyl hexanol. An initial reaction to form a monoester is fast, but the subsequent conversion of the monoester to diester is carried out by refluxing in the presence of the catalyst  
10 composition at a temperature of 180-200°C until all the water has been removed. Subsequently the excess alcohol is removed.

In an alcoholysis reaction, the ester, first alcohol and catalyst composition are mixed and, generally, the product alcohol (second alcohol) is removed by distillation, often as an  
15 azeotrope with the ester. Frequently it is necessary to fractionate the vapour mixture produced from the alcoholysis in order to ensure that the second alcohol is separated effectively without significant loss of product ester or first alcohol. The conditions under which alcoholysis reactions are carried out depend principally upon the components of the reaction and generally components are heated to the boiling point of the mixture used.

20 A preferred process of the invention is the preparation of polyethylene terephthalate. A typical batch production of polyethylene terephthalate is carried out by charging terephthalic acid and ethylene glycol to a reactor along with catalyst composition, if desired, and heating the contents to 260 - 270°C under a pressure of about 0.3 MPa. Reaction commences as the acid  
25 dissolves at about 230°C and water is removed. The product is transferred to a second autoclave reactor and catalyst composition is added, if needed. The reactor is heated to 285 - 310°C under an eventual vacuum of 100 Pa to remove ethylene glycol by-product during the ensuing polycondensation reaction. The molten product ester is discharged from the reactor, cooled and chipped. The chipped polyester may be then subjected to solid state  
30 polymerisation, if appropriate.

A preferred means of adding the catalyst compositions of this invention to a polyesterification reaction is in the form of a slurry or solution in the glycol being used (e.g. ethylene glycol in the preparation of polyethylene terephthalate). This method of addition is applicable to addition of

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the catalyst composition to the esterification reaction at the first stage or at the second polycondensation stage.

5 The amount of catalyst used in the esterification process of the invention generally depends upon the total metal content (expressed as amount of Ti, Zr or Al) of the catalyst composition. Usually the amount is from 0.1 to 1200 parts per million (ppm) of metal based on weight of product ester for direct or transesterification reactions. Preferably, the amount is from 1 to 650 ppm of total metal based on weight of product ester. In polyesterification reactions the amount used is generally expressed as a proportion of the weight of product polyester and is usually  
10 from 0.1 to 550 ppm expressed as total metal (Ti, Zr or Al) based on product polyester. Preferably, the amount is from 1 to 250 ppm, more preferably 3 to 100 ppm expressed as total metal based on product polyester.

15 The products of this invention have been shown to be effective catalyst compositions for producing esters and polyesters at an economical rate without leading to haze in the final product and with a reduced amount of yellowing of polyesters in comparison to known catalysts. They have also been shown to be stable against precipitation from polyester products when aqueous base or phosphoric acid is added to such products.

20 The invention is illustrated by the following examples.

#### Preparation of Organometallic Compounds for use in Catalyst Compositions

##### EXAMPLE 1

25 Ethylene glycol (49.6 g, 0.8 moles) was added from a dropping funnel to stirred titanium n-butoxide (34 g, 0.1 mole) in a 250 ml flask fitted with stirrer, condenser and thermometer. An aqueous solution of sodium hydroxide, containing 32% NaOH by weight, (6.25 g, 0.05 mole) was added to the reaction flask slowly with mixing to yield a clear yellow liquid. To this liquid was added a di (polyoxoethylene) hydroxymethyl phosphonate available  
30 under the trade name Victastab HMP from Akzo Nobel, (18.93 g, 0.052 mole of phosphorus). After removing n-butanol at 70°C under vacuum to constant weight the product was a liquid with a Ti content of 2.76% by weight.

##### EXAMPLE 2

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Ethylene glycol (49.6 g, 0.8 moles) was added from a dropping funnel to stirred titanium n-butoxide (34 g, 0.1 mole) in a 250 ml flask fitted with stirrer, condenser and thermometer. An aqueous solution of sodium hydroxide, containing 32% NaOH by weight, (6.25 g, 0.05 mole) was added to the reaction flask slowly with mixing to yield a clear yellow liquid. To this liquid was added an oligomeric phosphonate available under the trade name Fyrol 51 from Akzo Nobel, (7.852 g, 0.052 mole of phosphorus). After removing n-butanol at 70°C under vacuum to constant weight the product was a liquid with a Ti content of 6.64% by weight.

## 10 EXAMPLE 3

Ethylene glycol (49.6 g, 0.8 moles) was added from a dropping funnel to stirred titanium n-butoxide (34 g, 0.1 mole) in a 250 ml flask fitted with stirrer, condenser and thermometer. An aqueous solution of sodium hydroxide, containing 32% NaOH by weight, (6.25 g, 0.05 mole) was added to the reaction flask slowly with mixing to yield a clear yellow liquid. To this liquid was added diethyl-N,N-bis(2-hydroxyethyl)aminomethyl phosphonate available under the trade name Fyrol 6 from Akzo Nobel, (18.93 g, 0.074 mole of phosphorus). After removing n-butanol at 70°C under vacuum to constant weight the product was a liquid with a Ti content of 7.00% by weight.

## 20 EXAMPLE 4

Ethylene glycol (49.6 g, 0.8 moles) was added from a dropping funnel to stirred titanium n-butoxide (34 g, 0.1 mole) in a 250 ml flask fitted with stirrer, condenser and thermometer. An aqueous solution of sodium hydroxide, containing 32% NaOH by weight, (6.25 g, 0.05 mole) was added to the reaction flask slowly with mixing to yield a clear yellow liquid. To this liquid was added a triethylphosphonoacetate available under the trade name TEPA from Rhodia, (11.7 g, 0.052 mole of phosphorus). After removing n-butanol at 70°C under vacuum to constant weight the product was a liquid with a Ti content of 6.80% by weight.

## 30 EXAMPLE 5

Ethylene glycol (99.2 g, 1.6 moles) was added from a dropping funnel to stirred titanium n-butoxide (34 g, 0.1 mole) in a 250 ml flask fitted with stirrer, condenser and thermometer. An aqueous solution of sodium hydroxide, containing 32% NaOH by weight, (9.38 g, 0.075 mole) was added to the reaction flask slowly with mixing to yield a clear yellow liquid. To this liquid was added a dibutyl hydrogen phosphite available under the trade name DBHP from Rhodia,

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(10.1g, 0.052 mole of phosphorus). After removing n-butanol at 70°C under vacuum to constant weight the product was a liquid with a Ti content of 6.31% by weight.

**EXAMPLE 6 (Comparative)**

- 5 Citric acid monohydrate (132.5 g, 0.63 moles) was dissolved in water (92.8 g). To the stirred solution was slowly added titanium isopropoxide (72.0 g, 0.25 moles). This mixture was heated to reflux for 1 hour to yield a hazy solution. This solution was distilled under vacuum to remove free water and isopropanol. The product was cooled below 70°C and 32 %w/w aqueous sodium hydroxide (94.9 g, 0.76 moles) was added slowly to the stirred solution. The product was filtered, mixed with ethylene glycol (125.5 g, 2.0 moles) and heated under vacuum to remove free water/isopropanol. The product was a slightly hazy, very pale yellow liquid (Ti content 3.85 % by weight).

**EXAMPLE 7 (Comparative)**

- 15 Ethylene glycol (496.0 g, 8.00 moles) was added from a dropping funnel to stirred titanium n-butoxide (340 g, 1.00 mole) in a 1 litre fishbowl flask fitted with stirrer, condenser and thermometer. An aqueous solution of sodium hydroxide, containing 32% NaOH by weight, (125 g, 1.00 mole) was added to the reaction flask slowly with mixing to yield a clear pale yellow liquid. To this liquid was then added a butyl acid phosphate, (91.0 g, 0.50 mole of phosphorus) and the resulting mixture was stirred for 1 hour to produce a pale yellow liquid with a Ti content of 4.56% by weight.

**EXAMPLE 8 (Comparative)**

- 25 Ethylene glycol (136 g, 2.2 moles) was added from a dropping funnel to stirred titanium n-butoxide (34 g, 0.1 mole) in a 250 ml flask fitted with stirrer, condenser and thermometer. An aqueous solution of tetraethyl ammonium hydroxide (TEAH), containing 35% TEAH by weight, (5.26 g, 0.05 mole) was added to the reaction flask slowly with mixing to yield a clear yellow liquid. After removing n-butanol at 70°C under vacuum to constant weight the product was a liquid with a Ti content of 3.25% by weight.

**EXAMPLE 9 (Comparative)**

- 30 Ethylene glycol (136 g, 2.2 moles) was added from a dropping funnel to stirred titanium n-butoxide (34 g, 0.1 mole) in a 250 ml flask fitted with stirrer, condenser and thermometer. An aqueous solution of choline hydroxide (ChOH), containing 35% ChOH by weight, (g, 0.05 mole) was added to the reaction flask slowly with mixing to yield a clear yellow liquid. After

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removing n-butanol at 70°C under vacuum to constant weight the product was a liquid with a Ti content of 3.39% by weight.

#### USE OF CATALYSTS IN POLYESTERIFICATION REACTIONS

##### 5 EXAMPLE 10

A polycondensation reaction was carried out in a mechanically-stirred 300 ml glass vessel fitted with side arm and cold trap for collection of monoethyleneglycol. A thermostatically controlled ceramic heating element was used to provide heat and an oil vacuum pump was connected to the cold trap. A nitrogen blanket was provided via a connection to the cold trap.

10 Polyethylene terephthalate was prepared from pure bis(hydroxyethyl)- terephthalate polymer precursor. 100 g of bis(hydroxyethyl)terephthalate polymer precursor was placed in the reaction flask under a nitrogen flow, followed by a dilute solution of catalyst component in monoethyleneglycol. For the catalyst (Table 1) the level was set at 30ppm (based on metal content). This was heated with stirring to 250 °C for 20-25 minutes. The nitrogen flow was

15 stopped and vacuum applied steadily to 100 Pa. After 20-25 minutes the temperature was increased steadily from 250 °C to 290 °C. As the reaction progressed the current required to maintain a constant stirrer speed increased up to a specified torque reading, at which point the reaction was deemed to be complete. The vacuum was then broken with nitrogen and the molten polymer discharged and quenched into cold water. It was then dried for 12 hours at 65

20 °C.

##### EXAMPLE 11

The catalysts were used to prepare polyethylene terephthalate (PET). Ethylene glycol (2.04 kg) and terephthalic acid (4.55 kg) were charged to a stirred, jacketed reactor. The catalyst

25 and other additives were added and the reactor heated to 226 - 252 °C at a pressure of 40 psi to initiate the first stage direct esterification (DE) process. Water was removed as it was formed with recirculation of the ethylene glycol. On completion of the DE reaction the contents of the reactor were allowed to reach atmospheric pressure before a vacuum was steadily applied. The stabilisers were added and the mixture heated to 290 ± 2 °C. under vacuum to

30 remove ethylene glycol and yield polyethylene terephthalate. The final polyester was discharged once a constant torque had been reached which indicated an IV of around 0.62. The polymer was analysed and the results are shown in Table 2.

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Polymer Analysis

The colour of the polymer was measured using a Byk-Gardner Colourview spectrophotometer. A common model to use for colour expression is the Cielab L\*, a\* and b\* scale where the b-value describes yellowness. The yellowness of the polymer increases with b-value.

- 5 The polymer intrinsic viscosities were measured by glass capillary viscometry using 60/40 phenol/1,1,2,2-tetrachlorethane as solvent. The results are shown in Tables 1 - 2.
- Discharge of molten polymer from a reactor takes place over a period of time during which the polymer is held in the molten phase at elevated temperature. The time of discharge of the polymer was noted and is shown in the tables.

10

Table 1

Catalyst Example  30 ppm Ti	Reaction Time (Minutes)	Colour 30 mins		
		L*	a*	b*
1	120	62.8	-1.4	12.9
2	120	55.1	-0.4	15.9
3	120	60.2	-1.9	11.7
4	120	71.6	-1.2	13.4
5	120	56.9	-1.3	8.7

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Table 2

Catalyst	ppm Ti	ppm P			ppm Co	DE Time mins	PC Time mths	Total time mths	I.V.	5 minutes			30 minutes			% increase in b
		In Catalyst	As $H_3PO_4$	Total						L	a	b	L	a	b	
1	30	10	-	10	0	48	90	138	0.73	56.7	3.1	34.1	56.3	5.1	36.4	6.7
4	30	10	-	10	0	65	105	170	0.59	61.0	-3.2	25.7	54.5	1.5	30.5	18.7
2	30	10	-	10	0	58	85	143	0.59	65.7	-3.5	24.7	55.7	1.2	31.3	26.7
6 <sup>1</sup>	30	-	10	10	0	58	97	155	0.55	56.5	0.2	28.5	50.3	4.7	32.8	15.8
6 <sup>1</sup>	15	-	10	10	25	64	104	168	0.82	55.6	-1.9	11.0	57.2	-1.0	16.7	51.4
7 <sup>1</sup>	30	10	6	16	0	98	92	190	0.60	67.6	-2.2	11.22	66.8	-2.1	16.9	50.8
7 <sup>1,2</sup>	15	5	3	8	0	119	111	230	0.63	68.1	-3.1	12.2	61.2	-0.8	22.9	87.7
8 <sup>1,4</sup>	15	-	10 (DE)	10	25	62	112	174	0.62	68.4	-2.8	11.0	70.4	-2.7	15.0	38
8 <sup>1,5</sup>	15	-	10 (DE)	10	25	61	110	171	0.62	65.2	-2.6	10.7	66.6	-1.8	14.7	37
9 <sup>1,4</sup>	15	-	10 (DE)	10	25	64	108	172	0.62	62.4	-1.3	7.4	62.4	-1.4	11.5	55.4
TIPT <sup>1,3</sup>	15	-	10	10	25	65	118	183	0.62	68.1	-2.7	9.3	61	0.1	19.4	108.0

## Notes

<sup>1</sup> indicates a comparative catalyst.<sup>2</sup> Used with 150 ppm Sb as antimony acetate<sup>3</sup> TIPT = tetraisopropoxy titanium<sup>4</sup> Phosphorus compound added was Hordaphos<sup>TM</sup> MEG phosphate solution from Clariant AG at the beginning of the DE reaction<sup>5</sup> Phosphorus compound added was Hordaphos<sup>TM</sup> DGB(LP) from Clariant AG at the beginning of the PC reaction

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CLAIMS

1. A catalyst composition suitable for use as a catalyst for the preparation of an ester comprises an organometallic compound which is the reaction product of
  - i. an alkoxide or condensed alkoxide of at least one metal selected from titanium, zirconium or aluminium,
  - ii. an alcohol containing at least two hydroxyl groups,
  - iii. a base and
  - iv. an organophosphorus compound of general formula  $PX(OR^1)_a(R^2)_b$  where X is S or O,  $R^1$  is alkyl/aryl, substituted alkyl/aryl, ether-alkyl, alkoxy,  $-C(O)R^3$  where  $R^3$  is (optionally substituted)  $C_{1-6}$  alkyl or carboxylic acid (or derivative thereof),  $-(CH_2)_xCOOR^4$ , where  $R^4$  is alkyl, preferably  $C_{1-6}$  alkyl and x is preferably 1 – 3; each  $R^2$  is independently H, alkyl/aryl, substituted alkyl/aryl, ether-alkyl, e.g. polyoxyalkyl, especially polyoxyethyl or polyoxypropyl, alkoxy,  $-OCOR^3$  where  $R^3$  is (optionally substituted)  $C_{1-6}$  alkyl or carboxylic acid (or derivative thereof),  $-(CH_2)_xCOOR^4$ , where  $R^4$  is alkyl, preferably  $C_{1-6}$  alkyl and x is preferably 1 – 3; at least one of  $R^1$  and  $R^2$  contains a donor group which is capable of coordinating to or forming a covalent bond with the metal, a is in the range 1 – 3, b is in the range 0 – 2 and  $a + b = 3$ .
2. A catalyst composition according to claim 1 wherein the donor group is selected from S, O, N, OH, NH or SH.
3. A catalyst composition as claimed in claim 1 or claim 2, wherein the organophosphorus compound is a phosphite diester, phosphate triester or phosphonate diester.
4. A catalyst composition as claimed in claim 3, wherein the organophosphorus compound comprises a trialkylphosphonoacetate or di(polyoxyalkyl)hydroxyalkylphosphonate.
5. A catalyst composition as claimed in any of the preceding claims wherein said base is selected from sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, calcium hydroxide, ammonium hydroxide, tetrabutyl ammonium hydroxide, tetraethyl ammonium hydroxide (TEAH), choline hydroxide (trimethyl(2-hydroxyethyl)ammonium hydroxide) or benzyltrimethyl ammonium hydroxide, monoethanolamine, diethanolamine, triethanolamine and triisopropanolamine.



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6. A catalyst composition as claimed in any of the preceding claims wherein said alcohol is selected from 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-2,4-pentanediol, diethylene glycol, a polyethylene glycol, a polypropylene glycol, glycerol, trimethylolpropane or pentaerythritol.
7. A catalyst composition as claimed in any of the preceding claims wherein the amount of organophosphorus compound present provides from 0.1 to 4.0 moles of phosphorus to 1 mole of metal (titanium, zirconium or aluminium) in the composition.
8. A catalyst composition as claimed in any preceding claim, further comprising a compound of germanium, antimony or tin.
9. A process for the preparation of an ester comprising carrying out an esterification reaction in the presence of a catalyst composition as claimed in any one of claims 1 to 8.
10. A process as claimed in claim 9 comprising a direct esterification reaction between saturated and unsaturated monocarboxylic acids rosin acids, dicarboxylic acids, anhydrides of such acids and polycarboxylic acids with aliphatic straight chain and branched monohydric alcohols, dihydric alcohols or polyhydric alcohols.
11. A process as claimed in claim 10 wherein the acids and anhydrides are selected from stearic acid, isostearic acid, capric acid, caproic acid, palmitic acid, oleic acid, palmitoleic acid, triacontanoic acid, benzoic acid, methyl benzoic acid, salicylic acid, abietic acid, phthalic acid, isophthalic acid, terephthalic acid, sebacic acid, adipic acid, azelaic acid, succinic acid, fumaric acid, maleic acid, naphthalene dicarboxylic acid and pamolic acid, trimellitic acid, citric acid, trimesic acid, pyromellitic acid and anhydrides of these acids and the alcohols are selected from butyl, pentyl, hexyl, octyl and stearyl alcohols, 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol glycerol and pentaerythritol.
12. A process as claimed in claim 9 comprising a transesterification reaction between methyl, ethyl and propyl esters and butyl, hexyl, n-octyl and 2-ethyl hexyl alcohols and substituted alcohols such as dimethylaminoethanol.
13. A process as claimed in claim 9 wherein said process is a polyesterification reaction.

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14. A process as claimed in claim 13 comprising the reaction of a diacid or diester selected from terephthalic acid, dimethyl terephthalate, naphthalene dicarboxylic acid, dimethyl naphthalate or isophthalic acid with a diol selected from 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol or a polyhydric alcohol such as glycerol, trimethylolpropane or pentaerythritol.

15. A polyester material prepared by the process as claimed in claim 13 or claim 14.

## INTERNATIONAL SEARCH REPORT

PCT/GB 02/05281

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B01J31/12 C07F9/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B01J C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal

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X	EP 1 156 070 A (SK CHEMICALS CO., LTD., S. KOREA) 21 November 2001 (2001-11-21) paragraph '0010! - paragraph '0012!	4,8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex

## \* Special categories of cited documents:

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Name and mailing address of the ISA

European Patent Office, P.B. 5819 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Richter, H

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